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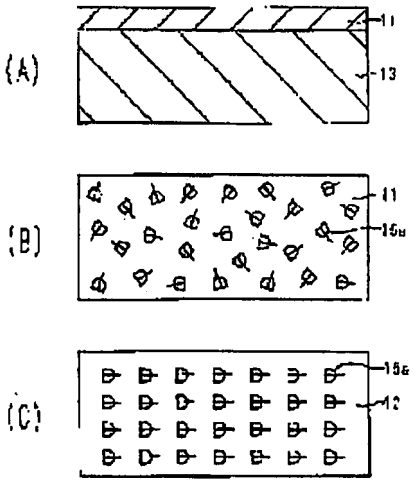
(54) RESIST FILM, ITS FORMING METHOD AND RESIST SOLUTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain sufficient degree of resolution by a method in which the orientation and the attitude of a number of resist molecules, constituting a resist film, are made uniform.
SOLUTION: Electrodes A and B are provided on one end and on the other end of the surface of the resist 11 on a wafer 13, and the second pair of electrodes C and D are formed on the surface in parallel with the surface of the wafer 13. Then, a DC current is allowed to flow between the electrodes A and B, and subsequently, a DC current is allowed to flow between the electrodes C and D. Electric field is applied from biaxial direction between the electrodes A and B, and C and D simultaneously or alternately while current value, voltage and current application item are being changed delicately. Subsequently, the wafer is dried up at 100°C, for example. Accordingly, the photosensitive functional group in a resist molecule 15a can be fixed facing to the expected surface to be exposed in the state in which the attitude of each resist molecule is being controlled. A pattern is formed on the fixed resist film 12, and a UV exposing operation is conducted from above a mask 17.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resist film, the formation approach of this resist film, and a resist solution.

[0002]

[Description of the Prior Art] Contraction-ization of the component dimension in a semiconductor device progresses in recent years, and micro processing, i.e., a quarter micron, and the processing technique not more than it will just be going to be required from now on also in the photolithography process which is one of the manufacture process of the. Reference (reference:) [Journal of Photopolymer Science and Technology.Volume 7, Number 3 (1994) pp.433-448,] [Environmentally] Stable Chemical Amplification Positive Resist ;P rinciple, Chemistry, Contamination Resistance, and and Lithographic According to Feasibility.Hiroshi ITO et al. As a resist which succeeded in the lithography by the 0.25 micrometers (quarter micron) KrF excimer laser stepper There was a resist called an ESCAP resist (Environmentally Stable Chemical Amplification Positive Resist). However, the resist film formed of these resists was applied on the wafer, thickness control was only carried out by the spin coat method etc., especially the control about orientation, a three-dimensional location, etc. of a resist molecule in the resist film was not made, but the resist molecule existed in the resist film in the almost random condition.

[0003] It explains briefly using drawing. Drawing 7 is the image Fig. of the resist film applied on the wafer having shown the formation approach of the conventional resist film roughly. (A) Drawing is a structure section Fig. at the time of forming the resist film 52 on a wafer 53, forming the mask 57 of the configuration corresponding to a desired pattern on the resist film 52, and exposure processing being completed. (B) Drawing is a superficial image Fig. when seeing the condition of the resist molecule 55 in the resist film 52 in the (A) Fig. and a coincidence point from the upper part. Resist molecule 55a of the exposed part (exposed field) 59 deteriorates, and it expresses that it is insoluble to a developer with insolubilization resist molecule 55b. (C) Drawing is a structure section Fig. at the time of a lithography process being completed. In this case, negative resist is used and the resist film 52 of the exposed field 59 of the (A) Fig. remains. The (D) Fig. shows the condition of insolubilization resist molecule 55b in this resist film 52. Within the resist film 52, since the resist molecule 55 exists in the random condition, the resist film 52 after exposure and a development is uneven in response to the effect of the location of a resist molecule, or the sense.

[0004]

[Problem(s) to be Solved by the Invention] Usually, the resist molecule which consists of 1000 molecular weight - a-100,000 number For example, since it is thought that it exists in width of face of 0.25 micrometers together with hundreds of piece irregularity from dozens of pieces, When processing the more detailed Rhine width of face below the quarter micron required of a resist Since the effect of the location of a resist molecule or the sense became large more, even if it processed using ultraviolet rays with short wavelength, an electron ray or an X-ray, etc., that the roughness and rudeness of a resist cross section after development remain was not that from which it is not avoided, therefore sufficient resolution is obtained.

[0005] For this reason, in detailed lithography processing, an appearance of resist film with which sufficient resolution is obtained, and its formation approach was desired.

[0006]

[Means for Solving the Problem] For this reason, the resist film of this invention is characterized by consisting of many resist molecules and having arranged each orientation and posture of a resist molecule of these large number.

[0007] For this reason, since a photosensitive functional group can be turned to the resist film front face exposed in phot lithography down stream processing performed behind, as a result of carrying out lithography processing of the above-mentioned resist film, the processed resist cross section becomes smooth and sufficient resolution is obtained.

[0008] Moreover, in the above-mentioned resist film, the location of a resist molecule is arranged further. For this reason, the resist cross section after lithography processing becomes smooth, and can raise resolution further.

[0009] Moreover, after the formation approach of the above-mentioned resist film applies electric field from biaxial and arranges many the orientation and the postures of a resist molecule in this resist solution to the resist solution applied on the wafer, it fixes these resist molecules.

[0010] By applying electric field by turns simultaneous from biaxial, in response to an electrophoresis-operation, each resist molecule in a resist solution is the same posture, and comes to turn to the fixed direction. For this reason, the resist film obtained by fixing a resist molecule in this condition Since the light of each resist molecule and the functional group which reacts can be turned to the exposed field of the resist film at the time of exposure of the phot lithography processing performed behind, As a result of being able to make most resist molecules of an exposure part react altogether and developing them, when it is a positive resist, an exposure part can be removed as a pattern (when it is negative resist, an exposure part can be made to remain as a pattern). . Therefore, also in micro processing, a resist cross section can become

smooth and can raise resolution.

[0011] Moreover, in the formation approach of this resist film, biaxial is passed along the core of a wafer and it is characterized by considering as biaxial [of the x axis which is a straight line within this wafer side and the y-axis which it passes along this core and is a straight line perpendicular to a wafer side].

[0012] Thus, biaxial is taken and the orientation and the posture of a resist molecule are controlled by the electric field of the biaxial direction of the direction of a x axis, and the direction of the y-axis. If a resist molecule is compared to human being's hand and explained, if electric field are applied in the direction of a x axis, suppose first that a fingertip turns to the fixed direction. Although the direction which the fingertip has turned to is arranged in 1 shaft orientations, if some which are upwards suitable have a palm, it will be in a condition which some which have turned to the bottom have. Next, if electric field are applied in the direction of the y-axis, palms can be turned upwards all at once. Thus, if a resist molecule is controlled applying electric field in the biaxial direction, the posture of each molecule is controllable. Therefore, it becomes possible to make an exposure side turn and carry out orientation of the photosensitive functional group of a resist molecule.

[0013] Moreover, after the resist film applies electric field from 3 shaft orientations and arranges the orientation, posture, and location of a resist molecule to the resist solution applied on the wafer, it fixes the resist molecule of these large number.

[0014] By applying the electric field of the biaxial direction to a resist solution, as already explained, the posture of a resist molecule is controllable. By furthermore applying electric field from another direction, the method of a list of resist molecules in every direction, i.e., an array location, is controllable. Consequently, the resist cross section after exposure and a development can be formed more smoothly, and resolution can be raised further.

[0015] this -- a resist -- the film -- formation -- an approach -- setting -- three -- a shaft -- a wafer -- a core -- a passage -- this -- a wafer -- a field -- inside -- a straight line -- it is -- a x axis -- this -- a wafer -- a core -- a passage -- a wafer -- a field -- being perpendicular -- a straight line -- it is -- the y-axis -- a x axis -- and -- the y-axis -- intersecting perpendicularly -- a straight line -- it is -- the z-axis -- it is characterized by considering as three shafts.

[0016] Thus, the orientation, posture, and location of a resist molecule are controlled by taking three shafts and applying electric field from 3 of a x axis, the y-axis, and the direction of the z-axis directions.

[0017] Like above-mentioned explanation, if a resist molecule is compared to human being's hand and explained, a palm will be turned upwards, and each hand (resist molecule currently controlled by the electric field of the biaxial direction) that the

fingertip is suitable in the fixed direction exists in various locations in space. Then, if electric field are applied from another direction, orientation and a posture can determine the location in space, while it had been controlled. Thus, to the formed resist film, the resist cross section which remains by performing exposure and a development by a certain pattern becomes smoother, and can expect the further improvement in resolution.

[0018] When applying electric field from biaxial in forming the resist film on a wafer, moreover, as the formation approach It faces across the process which applies a resist solution on a wafer, the process which prepares the electrode for the directions of a x axis of the 1st pair in the front face of a resist solution on both sides of a wafer, and the front face of the above-mentioned resist solution. The process which prepares the electrode for the directions of the y-axis of the 2nd pair in the vertical side distant in parallel and spatially to this resist front face, It is characterized by including the process which energizes a direct current by turns simultaneous to the electrode for these directions of a x axis, and the electrode for the directions of the y-axis, and the process which dries the wafer with which the resist solution is applied.

[0019] According to this approach, by energizing two pairs of electrodes coincidence or by turns, it can move a resist molecule delicately and it not only turns the functional-group part of a resist molecule in the specific direction, but can carry out attitude control.

[0020] Moreover, the formation approach of the resist film in the case of applying electric field from 3 shaft orientations It faces across the process which applies a resist solution on a wafer, the process which prepares the electrode for the directions of a x axis of the 1st pair in the front face of a resist solution on both sides of a wafer, and the front face of the above-mentioned resist solution. The process which prepares the electrode for the directions of the y-axis of the 2nd pair in the vertical side distant in parallel and spatially to this resist front face, The process which prepares the electrode for the directions of the z-axis of the 3rd pair in the resist front face of a direction which intersects perpendicularly with the above-mentioned x-axis direction on both sides of a wafer, The process which energizes a direct current by turns simultaneous to the electrode for these directions of a x axis, and the electrode for the directions of the y-axis and the electrode for the directions of the z-axis, and the process which dries the wafer with which the resist solution is applied are included.

[0021] The resist molecule by which attitude control was carried out can be moved now by this, and the location in the resist film can be arranged.

[0022] Moreover, as a whole, it is neutrality mostly and what it is hard to move even if it applies electric field depending on a resist molecule can consider a certain thing. So, in this invention, an electrolyte is added to the resist molecule in a resist solution.

[0023] The added electrolyte bears the work which it is electrified [of plus or minus] in a resist solution, and helps migration of a resist molecule. Thus, if electric field are applied from biaxial or 3 shaft orientations to this resist solution applied to the wafer after adding an electrolyte to a resist molecule, it will become possible to control the orientation of the resist molecule which was hard to move, and a posture and a location.

[0024] Moreover, let an above-mentioned electrolyte be oligopeptide. Thereby, electrophoresis-migration of a resist molecule can be urged without barring the function as resist film.

[0025]

[Embodiment of the Invention] Hereafter, with reference to drawing, it explains per gestalt of operation of the resist film of this invention. In addition, each drawing is roughly shown in extent which can understand this invention. Moreover, in the following explanation, although a specific ingredient and specific conditions are used, it does not pass over these ingredient and conditions for the example of a suitable operation gestalt, therefore they are not limited to this at all by this invention.

[0026] <the gestalt of the 1st operation> -- how to form the resist film of this invention is first explained with reference to drawing 1 , drawing 2 , drawing 3 , and drawing 5 . Drawing 1 and drawing 2 consist of a sectional view which expressed the process used as the description of this invention roughly, and a superficial image Fig. showing the condition of the resist molecule in the resist film in each process. Moreover, drawing 3 and drawing 5 are rough structural drawings of the equipment for forming the resist film of this invention.

[0027] In this invention, the spin coat of LMR (a resist is only called the low-molecular naphthoquinonediazide sulfonate of a resist Low Molecular Weight Resist : cresol mold novolak and the following.)11 is first dropped and carried out to the 3 inch wafer (however, 1 inch about 2.54cm) 13 as a resist solution for 2000rpm (revolutions per minute) 30 minutes (drawing 1 (A)). Moreover, the (B) Fig. shows the condition of resist molecule 15a in the resist 11 at this time.

[0028] Next, an electrode is attached in the front face of the resist 11 on a wafer 13 (refer to drawing 3). When the cage hula (orientation flat) of a wafer 13 is turned down, Electrodes A and B are installed in the end of the straight line (here, let this straight line be a x axis.) which extends in right and left passing through the core of a wafer 13, and the other end (drawing 3). Preferably, the electrodes A and B of these 1st pair are installed by the method as shown in drawing 5 , respectively. That is, buffer solution 23 is put in in the container 21 with which the electrode 25 is installed in the pars basilaris ossis occipitalis, and the filter paper-like matter 27 which connects a resist 11 from a container 21 is formed. Buffer solution 23 has permeated

this filter paper-like matter 27, and a current flows to a resist 11 through the filter paper-like matter 27. Therefore, Electrodes A and B will consist of buffer solution 23, an electrode 25, and filter paper-like matter 27.

[0029] Next, the electrode of the 2nd pair is formed in a field (the upper part and field on a background) parallel to the field of a wafer 13. Here, an upper electrode is set to C and the electrode on a background is set to D (drawing 3). The electrodes C and D of these 2nd pair pass along the core of a wafer 13, are perpendicular to a wafer side and establish it on the y-axis which intersected perpendicularly with the x axis.

[0030] Next, a direct current (100V and 20mA) is passed among Electrodes A and B. The resistance welding time is set as arbitration. A direct current is energized among Electrodes C and D after this. And electric field are applied to a resist 11 from biaxial, changing delicately a current value, an electrical potential difference, and the resistance welding time coincidence or by turns between C and D between Electrodes A and B. Here, in order for conditions, such as a current value, and an electrical potential difference, the resistance welding time, to change with the magnitude of a wafer, the class of resist, a solvent, etc., they need to experiment each time and need to change conditions.

[0031] Then, this wafer is dried at 100 degrees C in a hot plate, oven, etc. By this, with the posture of each resist molecule 15a controlled, if it puts in another way, it can be made to be able to turn [functional group / in resist molecule 15a / photosensitive] to an exposure schedule side, and it can be fixed. Drawing 1 (C) is an image Fig. in the condition of a resist molecule that orientation and a posture were controlled within the resist film 12. In addition, the resist 11 used as the resist film 12 what was fixed by desiccation processing on the wafer 13.

[0032] Next, it is 20 mJ/cm2 by the upper part of the mask 17 after forming the mask 17 corresponding to a pattern to form on this resist film 12 to UV exposure machine. A light energy exposure is performed (drawing 2 (A)). After that, with a chlorobenzene, a development is performed for 30 seconds and a rinse is carried out for 30 seconds by the cyclohexane. Next, 100 degrees C is dried with a hot plate for 2 minutes. If the part with which the resist film 12 is not covered with a mask 17 if drawing 2 (A) and (B) are referred to is made into the exposed field 19, after exposure, the resist molecule of the exposed field 19 will deteriorate and will become insoluble at a developer (drawing 2 (B)). 15b shows an insolubilization resist molecule among drawing. Next, if negatives are developed, the resist film 12 of the pattern of drawing 2 as shown in (C) will be obtained, and it will be thought that insolubilization resist molecule 15b in the resist film 12 at this time is in a condition like drawing 2 (D). Since the orientation and the posture of resist molecule 15a and insolubilization resist 15b were controlled (drawing 1 (C)), after detailed lithography processing, the resist

film cross section is smooth, consequently succeeded in resolving of 0.20micromL/S (Rhine and tooth space).

[0033] The example to which electric field are applied from 3 shaft orientations to the resist solution on a wafer as a gestalt of <gestalt of the 2nd operation> the 2nd operation is explained with reference to drawing 4 .

[0034] The spin coat of the resist 11 is dropped and carried out to the 3 inch wafer 13 like the gestalt of the 1st operation, and the electrodes C and D of the 2nd pair are formed in the front face of a resist 11 on the upper part of the electrodes A and B of the 1st pair, and a wafer 13, and a background. The straight line which ties the electrodes A and B of the front face of a resist 11 after that, and a straight line which crosses a right angle at the core of a wafer 13 install the electrodes E and F of the 3rd pair in the part (when a cage hula is turned down, it is the edge of an up-and-down wafer) which arrives at the edge of a wafer 13 (resist front face) (drawing 4). The electrodes E and F of these 3rd pair pass along the core of a wafer 13, and establish it on the z-axis which intersects perpendicularly with a x axis and the y-axis.

[0035] next, between Electrodes A and B, between Electrodes C and D, and between Electrodes E and F -- respectively -- one by one -- or a sink and electric field are changed to coincidence in a direct current -- making -- a resist molecule -- orientation -- it is made to move Thereby, the functional group of a resist molecule can be turned to the exposure side at the time of carrying out exposure processing performed behind. Next, the wafer with which the resist was applied is heated and dried at 100 degrees C using a hot plate, oven, etc. Consequently, the photosensitive functional group of resist intramolecular can be fixed while the exposure schedule side had been made to turn to, and it can control to the location of a molecule further.

[0036] Next, if the mask corresponding to a desired pattern is prepared on the resist film and exposure and a development are performed like the gestalt of the 1st operation, a pattern with more high resolution can be obtained.

[0037] As a gestalt of <gestalt of the 3rd operation> the 3rd operation, the example which makes an electrolyte add to a resist molecule is explained with reference to (A) of drawing 6 , and (B). Drawing 6 is a superficial image Fig. showing the condition of the resist molecule within a resist.

[0038] Since it is a giant molecule, it bends depending on the resist molecule 31, a radical with a charge is located inside a resist molecule, and structure has what has difficult carrying out electrophoresis-actuation. The condition of such a resist molecule 31 is shown in the (A) Fig. of drawing 6 . For this reason, after making the electrolytes 33, such as oligopeptide, add to the resist molecule 31 and changing pH of a solvent further for example, orientation, and the posture and location of the resist molecule 31 which are hard to move are controllable by applying electric field from

the biaxial direction or 3 shaft orientations.

[0039]

[Effect of the Invention] Thus, since the orientation and the posture of a resist molecule within that film are controlled, as a result of the obtained resist film performing detailed lithography using this resist film, the cross section where the resist film was processed turns into a smooth field evenly. So, sufficient resolution can obtain also in micro processing below a quarter micron.

[0040] Moreover, if the resist molecule in a resist solution is fixed and the resist film is formed after applying electric field to the resist solution applied to the wafer from the biaxial direction or 3 shaft orientations, as explained above, the resist molecule in the resist film can also control the orientation, and a posture and a location. That is, sufficient resolution can be obtained as a result of most resist molecules of an exposure part reacting altogether since it becomes possible to make an exposed field turn to, and developing the photosensitive functional group of each resist molecule at the time of exposure of the phot lithography processing performed behind.

[0041] Moreover, in the resist solution applied to a wafer, if the electrolyte is made to add to the resist molecule in a solution, this electrolyte will be electrified within a resist solution and what electrophoresis-actuation (migration) of the resist molecule when applying electric field is helped for (it urges) will be made. Therefore, the orientation of the resist molecule which is hard to move, and a posture and a location are controllable.

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.

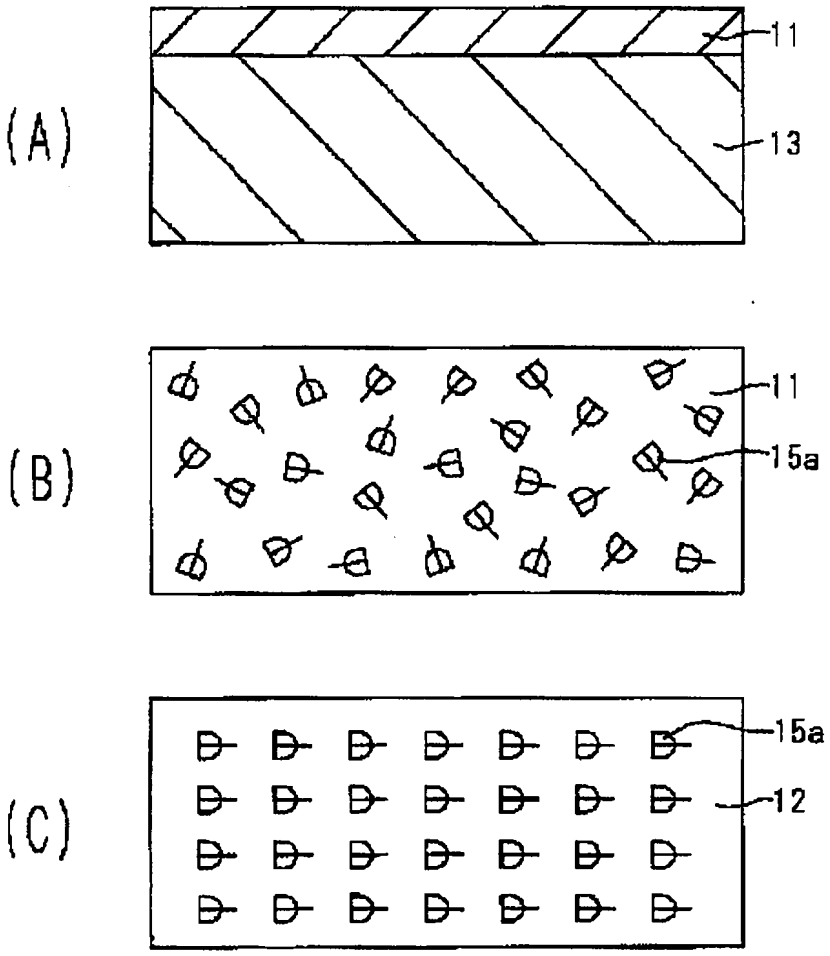
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Resist film characterized by having arranged the orientation and the posture of a resist molecule of said large number in the resist film which consists of many resist molecules.
[Claim 2] Resist film further characterized by having arranged the location of the resist molecule of said large number in the resist film according to claim 1.
[Claim 3] The formation approach of the resist film characterized by fixing the resist molecule of these large number after applying electric field from biaxial and arranging many the orientation and the postures of a resist molecule in this resist solution to the resist solution applied on the wafer.
[Claim 4] being according to claim 3 -- a resist -- the film -- formation -- an approach -- setting -- said -- biaxial -- said -- a wafer -- a core -- a passage -- this -- a wafer -- a field -- inside -- a straight line -- it is -- a x axis -- this -- a core -- a passage -- said -- a wafer -- a field -- being perpendicular -- a straight line -- it is -- the y-axis -- biaxial -- ** -- carrying out -- things -- the description -- ** -- carrying out -- a resist -- the film -- formation -- an approach .
[Claim 5] The formation approach of the resist film characterized by fixing the resist molecule of these large number after applying electric field from 3 shaft orientations and arranging much the orientation, postures, and locations of a resist molecule in this resist solution to the resist solution applied on the wafer.
[Claim 6] being according to claim 5 -- a resist -- the film -- formation -- an approach -- setting -- said -- three -- shafts -- said -- a wafer -- a core -- a passage -- this -- a wafer -- a field -- inside -- a straight line -- it is -- a x axis -- this -- a core -- a passage -- said -- a wafer -- a field -- being perpendicular -- a straight line -- it is -- the y-axis -- said -- a x axis -- and -- the y-axis -- intersecting perpendicularly -- a straight line -- it is -- the z-axis -- three -- shafts -- ** -- carrying out -- things -- the description -- ** -- carrying out -- a resist -- the film -- formation -- an approach .
[Claim 7] In forming the resist film on a wafer, it faces across the process which applies a resist solution on said wafer, the process which prepares the electrode for the directions of a x axis of the 1st pair in said resist solution front face on both sides of said wafer, and said resist solution front face. The process which prepares the electrode for the directions of the y-axis of the 2nd pair in the vertical side distant in parallel and spatially to this resist front face, The formation approach of the resist film characterized by including the process which energizes a direct current by turns simultaneous to the electrode for said directions of a x axis, and the electrode for the directions of the y-axis, and the process which dries the wafer with which said resist solution is applied.
[Claim 8] In forming the resist film on a wafer, it faces across the process which applies a resist solution on said wafer, the process which prepares the electrode for the directions of a x axis of the 1st pair in said resist solution front face on both sides of said wafer, and said resist solution front face. The process which prepares the electrode for the directions of the y-axis of the 2nd pair in the vertical side distant in parallel and spatially to this resist solution front face, The process which prepares the electrode for the directions of the z-axis of the 3rd pair in said resist solution front face of a direction which intersects perpendicularly with said direction of a x axis on both sides of said wafer, the electrode for said directions of a x axis, the

electrode for the directions of the y-axis, and the electrode for the directions of the z-axis -- coincidence -- or the formation approach of the resist film characterized by including the process which energizes a direct current one by one, and the process which dries the wafer with which said resist solution is applied.
[Claim 9] The resist solution characterized by having added the electrolyte to the resist molecule in a resist solution.
[Claim 10] The resist solution characterized by making said electrolyte into oligopeptide in a resist solution according to claim 9.

[Translation done.]



11：レジスト（レジスト溶液、ＬＭＲ）　12　：レジスト膜
13：ウェハ　15a：レジスト分子

この発明のレジスト膜の形成方法（その１）

Fig. 1

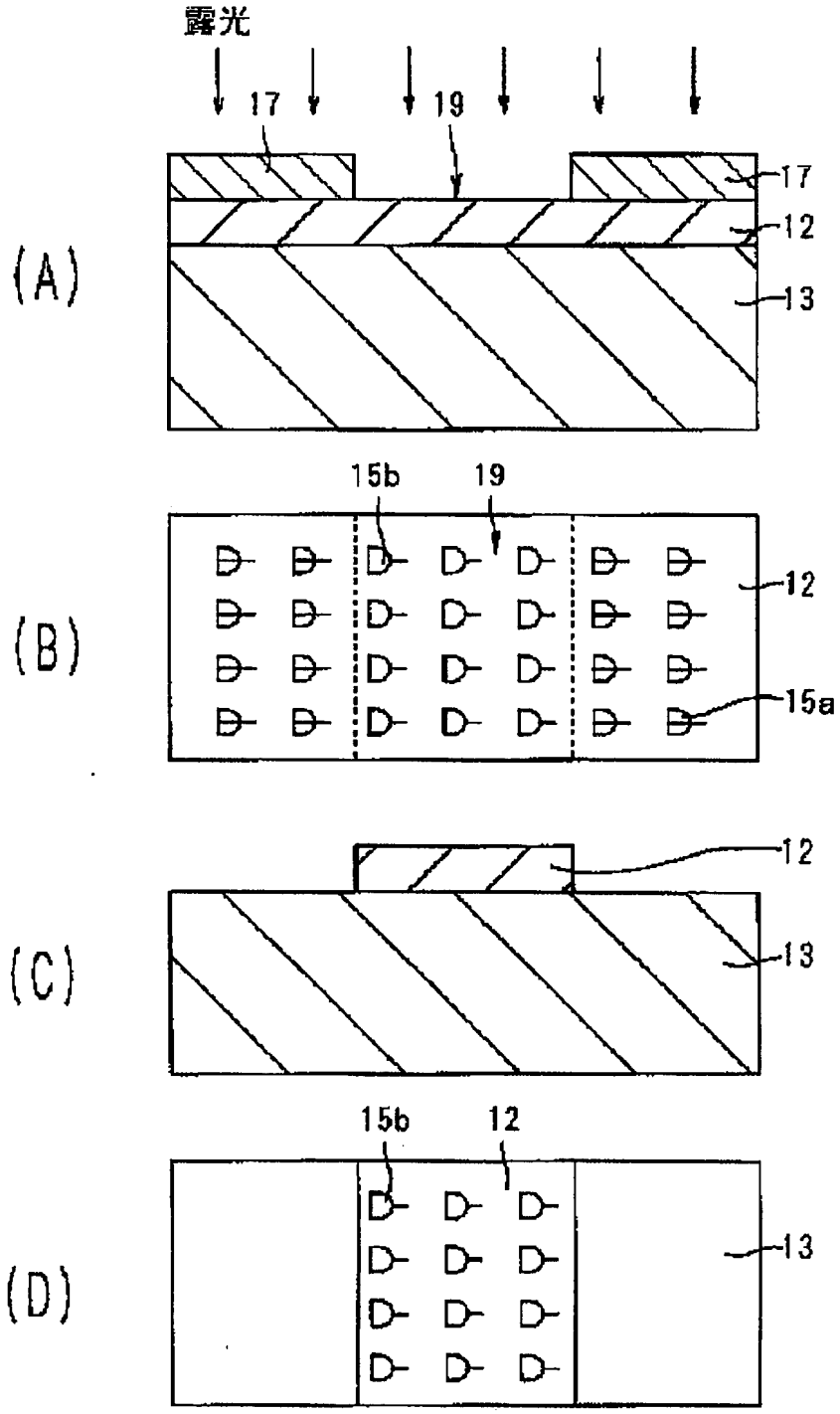
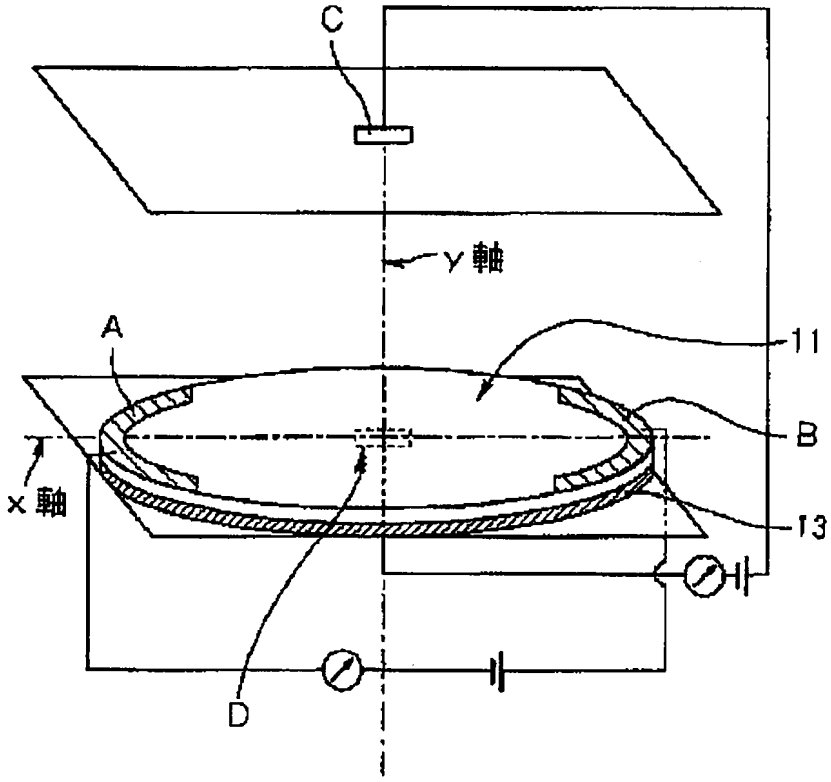


Fig. 2

15b：不溶化レジスト分子　　17：マスク
19　：被露光面

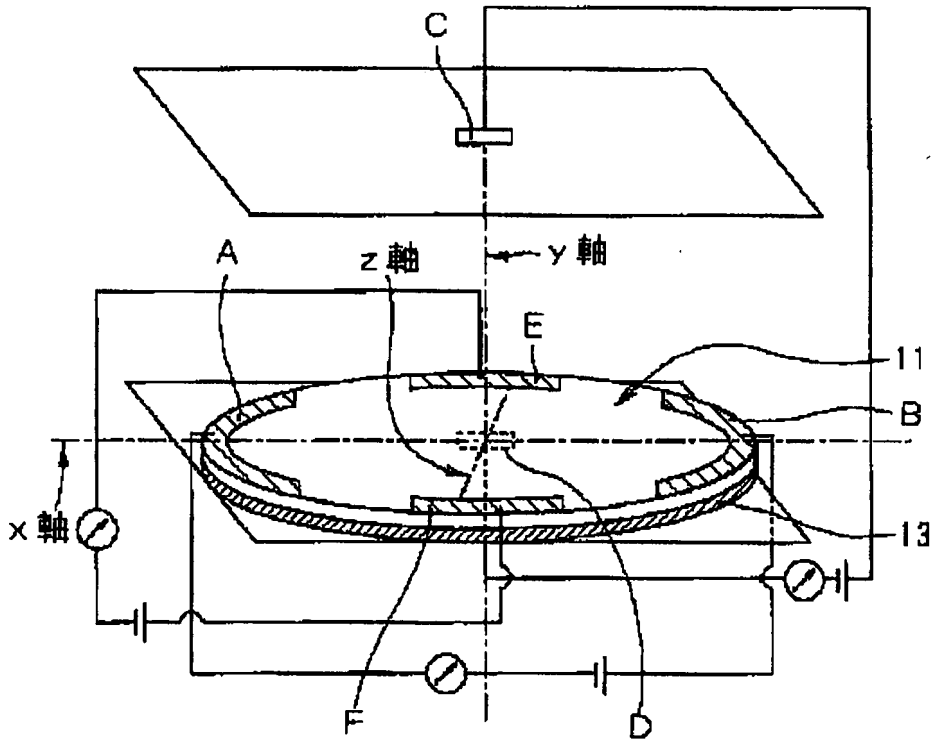
この発明のレジスト膜の形成方法（その２）



A，B：x 軸方向用の電極（第 1 対目の電極）
C，D：y 軸方向用の電極（第 2 対目の電極）

第 1 の実施の形態

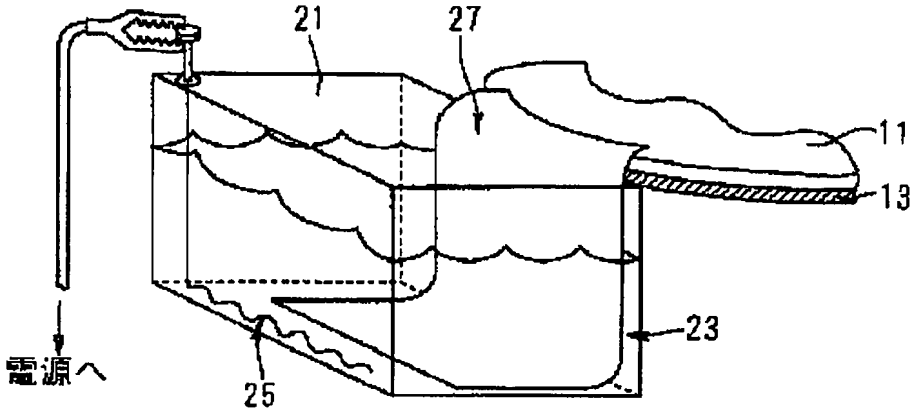
Fig. 3



E，F：z 軸方向用の電極（第３対目の電極）

第２の実施の形態

Fig. 4

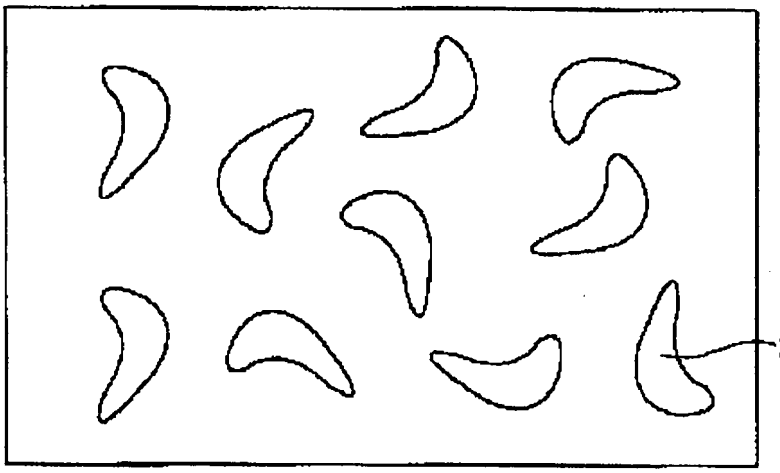


21：容器　　23：緩衝溶液
25：電極　　27：ろ紙状物質

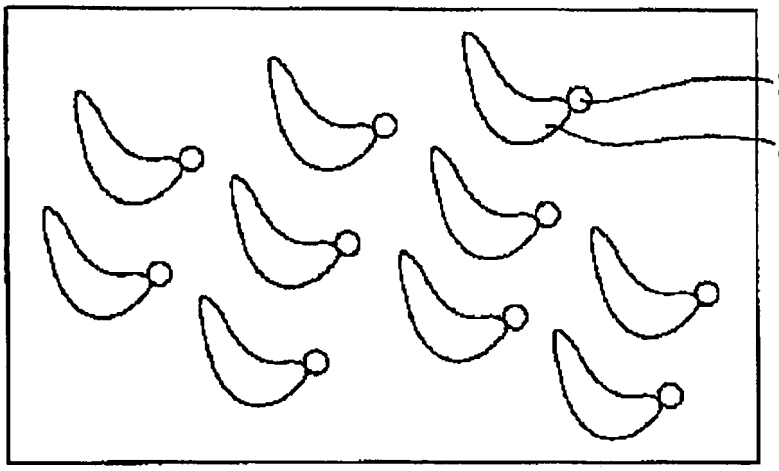
電極（A，B，EおよびF）の設置部分の概略図

Fig. 5

(A)



(B)

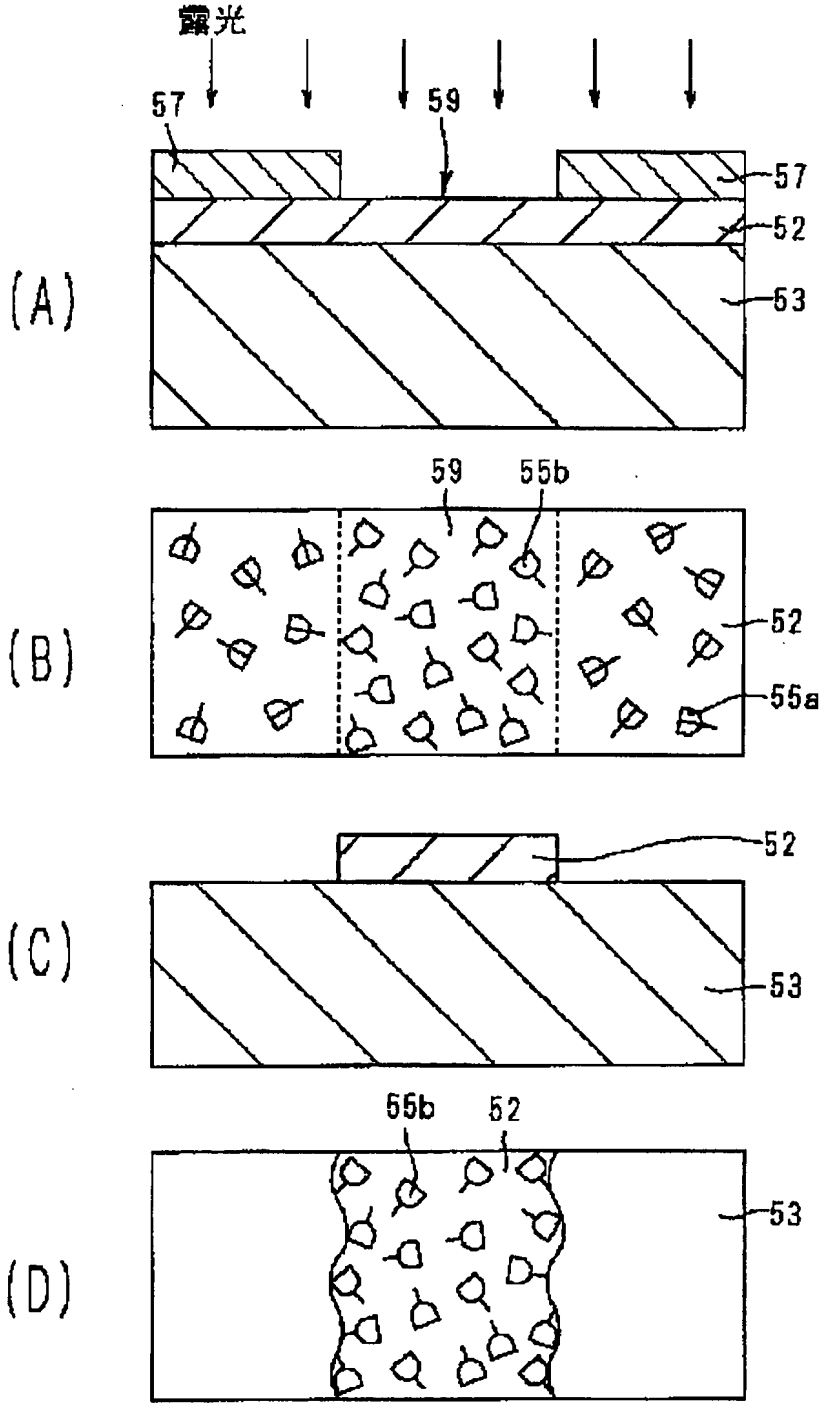


31：移動しにくいレジスト分子

33：電解質（オリゴペプチド）

第３の実施の形態

Fig. 6



従来のレジスト膜の形成方法

Fig. 7